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POLARIZATION AND INTERNAL RESISTANCE OF A GALVANIC CELL.

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THE electromotive force of many cells decreases very rapidly upon closed circuit, and after a period of rest it nearly recovers its original value. In some cells this is so marked that they are called "open circuit" cells. This is rather a conventional use. It means only that the cells cannot be used on closed circuit any considerable length of time. Carhart, in his *Primary Batteries*, gives curves for change in electromotive force, current, and internal resistance of a great many such cells. The cells are run for a certain period, and then allowed to recover for the same length of time. The total electromotive force, E , and fall of potential, E' , over a known external resistance, R , are measured. The current can be calculated from the equation $C = \frac{E'}{R}$, and the internal resistance, r , is determined from the equation $r = \frac{E - E'}{E'} \cdot R$.

While this method reveals the fact and magnitude of polarization, it by no means localizes it. That is, it does not tell us how much polarization occurs at each electrode. In cells of the Leclancé type it has generally been assumed that the polarization occurs at the carbon electrode, and that the potential difference between zinc and solution is constant. The fall in electromotive force on closed circuit, at first rapid, has generally been attributed to the formation of gas liberated from the positive ion at the carbon electrode. The later decrease would therefore be slower, owing to the slow absorption of gas at the carbon. Depolarizers are therefore frequently added to minimize the formation of gaseous products. On the other hand, when the cell is thrown on open circuit, it was reasoned that the gas actually in contact with the electrode would be rapidly given off,

and thus occasion a rapid rise in electromotive force. However, the gas somewhat removed from the electrode surface would hinder the electromotive force from regaining its original value for some time. The following short experiment was carried out with the view of substantiating or of refuting this explanation.

A diamond carbon cell was taken. This is essentially a Leclancé cell with no depolarizer. Reliance is had upon the soft carbons to absorb the gas and communicate it ultimately to the air. The carbon electrode consisted of seven pencils, each 9 mm. in diameter, arranged in a circle 75 mm. in external diameter. The zinc electrode, 6 mm. in diameter, is located symmetrically as to the carbons. For the purpose of this experiment the zinc electrode was displaced 4.5 mm. from the center, and diametrically opposite it at the same distance from the center was placed a special carbon electrode of exactly the same electrode surface. The end of this carbon protruding from the solution was copper plated, and a wire was soldered to it for making connections. A fresh solution of chemically pure ammonium chloride, containing five ounces to the quart, constituted the electrolyte.

The object of the experiment was to measure the electromotive force and its changes upon closed and open circuit between the zinc and main carbons, to get the electromotive force between the zinc and special carbon at intervals, and also to obtain the electromotive force of the carbon series during the progress of the experiment. Such a procedure would evidently enable one to determine the amount of polarization at the electrodes of the main circuit, provided the tension of the special carbon remained constant. Taking off appreciable currents through the special carbon as a circuit is manifestly excluded. It became necessary, therefore, to use a condenser. Even the charging of the microfarad condenser at first disturbed the potential differences, and no carbon could be found which would show a zero electromotive force between the main carbons and special carbon. At last a strip of glass 2 mm. thick and 18 mm. wide was inserted between the zinc and special carbon, whose surface was only 3 mm. from the former at the nearest point. Repeated charging and discharging of the condenser now showed no change in the potential differences in different parts of the circuit. The special carbon ultimately used was taken from another similar cell and turned down to proper size. Its electromotive force in respect to the main carbons was $+0.261$ volts.

Figure 1 shows the arrangement of the connections. The zinc and special carbons are designated by *a* and *b*, respectively. The keys K_1 , K_2 , K_3 , and K_4 are turned over by a pendulum swinging from left to right.¹ The time required for the pendulum to pass from K_1 to K_4 was about

¹ Carhart, PHYSICAL REVIEW, Vol. II., p. 392.

0.1 second. Keys c , d , and e make contact at the upper points unless depressed. By setting keys K_2 and K_3 only, and releasing the pendulum from its detent, we obtain the electromotive force of the main circuit, if c , d , and e are not disturbed. Had c been depressed, it would have given us the potential between the carbon electrodes, or had e instead of c been depressed, we should have obtained the total electromotive force of the zinc and special carbon circuit. It is evident that when keys K_1 , K_2 , K_3 , K_4 are set, and keys c and d are depressed,

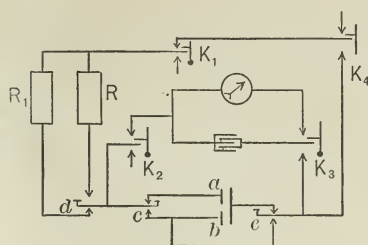


Fig. 1.

we can measure the fall of potential over R_1 . Under these conditions the special carbons and main carbons compose the battery. We can also measure the fall of potential over R , when either of the other two circuits is closed, by setting K_1 , K_2 , K_3 , and K_4 . R and R_1 were resistances of 1 ohm and 10 ohms respectively.

At the outset, repeated observations were taken upon the various circuits closed through the resistance R and R_1 for the above short-time period, 0.1 of a second. The ballistic galvanometer gave constant deflections in every case. Had there been a change of 0.5 mm. in the deflection, it could have been detected. To make a run upon the battery, the key K_1 was left in contact with the upper point, and key K_4 was set. In getting the total electromotive force of any circuit, it now becomes necessary to drop the detent to K_4 just before the liberated pendulum reaches key K_2 . Key K_4 must promptly be set again. With a little practice the time required for this operation need not exceed two seconds. In measuring the fall of potential over R and R_1 , open circuit was entirely avoided by stopping the pendulum with the hand before reaching key K_4 . Depressing the keys c and d or e also opens the circuit, but the time is here also small, as they need only be depressed while the pendulum is making one swing from left to right. This only required one-half second. The time the battery was upon open circuit, during the run of thirty minutes, was therefore very small. Upon recovery key K_4 was set only when terminal potential was to be determined. Key K_1 was then also set, and the battery would therefore only be closed for 0.1 of a second.

In the table of results E , E_s , and E_c represent total electromotive forces upon the main circuit, the zinc and special carbon circuit, and the main carbon and special carbon circuit, respectively. E' , E_s' , and E_c' represent the corresponding terminal potentials. The latter is measured over R_1 , which it became necessary to use in order to obtain appreciable readings

for E_c' . We will designate the internal resistances of circuits giving E , E_s , and E_c by r , r_s , and r_c , respectively. The resistance, r , began at 0.12 ohms and ended at 0.09. The resistance, r_s , began at 1.27 ohms, reached the value

TABLE I.
POLARIZATION.

Standard Clarke gave a deflection on the galvanometer = 80 = 1.434 volts.

Time.	E	E'	E_c	E_c'	E_s	E_s'
min. sec.						
0 00	1.368	1.020	+0.261	-0.144	1.614	0.738
0 15	—	1.017	—	—	—	—
1 00	1.260	—	—	—	—	—
1 45	—	1.013	—	—	—	—
2 45	—	1.011	—	—	—	—
3 30	—	—	0.395	—	—	—
4 15	1.206	—	—	—	—	—
5 30	—	1.010	—	—	—	—
6 30	—	—	—	0.045	—	—
7 30	1.161	—	—	—	—	—
8 00	—	1.004	—	—	—	—
8 30	—	—	—	0.054	—	—
9 30	—	—	0.450	—	—	—
10 00	—	1.004	—	—	—	—
11 00	—	—	—	—	1.647	—
11 45	—	—	—	—	—	0.558
14 30	—	0.990	—	—	—	—
15 30	1.062	—	—	—	—	—
17 00	—	—	—	0.101	—	—
19 00	—	0.962	—	—	—	—
19 30	1.071	—	—	—	—	—
21 00	—	—	—	—	1.623	0.603
23 45	—	—	—	—	—	—
27 00	—	—	—	0.102	—	—
28 00	—	—	0.531	—	—	—
29 00	—	—	—	—	1.602	—
30 00	1.008	—	—	—	—	—
31 00	—	0.927	—	—	—	—

of 1.7 ohms in 24 minutes, and ultimately fell to 0.78 ohms. The variation in r_c was more marked. At first it was 7.3 ohms. The next reading gave 88 ohms. During the recovery readings this resistance was of the same magnitude as at first. We attributed this great variation to some experi-

mental error which had escaped our notice. It is apparent that the internal resistances are of the relative magnitudes 1, 10, and 80. The one to ten ratio could be attributed to the decreased carbon electrode surface and the

TABLE II.
RECOVERY.

Time.	E	E'	E_c	E_c'	E_s	E_s'
min. sec.						
0 30	—	0.972	—	—	—	—
1 00	1.062	—	—	—	—	—
1 15	—	—	—	—	1.656	—
1 30	—	—	-0.522	—	—	—
2 00	—	—	—	-0.279	—	—
2 30	1.098	—	—	—	—	—
3 30	—	1.008	—	—	—	—
4 30	—	—	—	—	1.674	—
5 30	—	—	—	—	—	0.864
7 00	—	—	0.495	—	—	—
7 30	—	—	—	0.279	—	—
9 30	1.152	—	—	—	—	—
11 00	—	1.053	—	—	—	—
13 00	—	—	0.468	—	—	—
15 00	—	—	—	0.270	—	—
16 00	1.170	—	—	—	—	—
16 45	—	—	—	—	1.680	—
17 30	—	—	—	—	—	0.900
26 30	—	1.107	—	—	—	—
27 00	—	—	—	—	1.680	—
27 30	—	—	—	—	—	0.918
28 00	—	—	0.414	—	—	—
28 30	—	—	—	0.243	—	—
29 00	1.224	—	—	—	—	—
29 30	—	—	0.396	—	—	—
30 00	—	1.109	—	—	—	—
77 00	1.242	—	—	—	—	—
77 30	—	1.152	—	—	—	—
78 00	—	—	0.360	—	—	—
78 30	—	—	—	0.243	—	—
79 00	—	—	—	—	1.680	—
79 30	—	—	—	—	—	0.954

insertion of the glass plate. This does not help us in the one to eighty ratio. Now Carhart has shown¹ that the internal resistance varies with the

¹ See previous reference.

current. An introduction of 100 ohms in the main circuit would reduce the current to the same magnitude as the current in the E_c' circuit. To obtain appreciable differences in the readings for E and E' with this resistance in circuit, the connections were changed. The galvanometer was placed in series with 30,000 ohms and the battery. This gave a deflection of 366 scale divisions. When the battery was shunted with 100 ohms, the deflection was 362. This gives an internal resistance of 1.1 ohms, and the ratio is now about $\frac{1}{7}$ to $\frac{1}{7.5}$. With the galvanometer connected in this manner, a readable deflection could be obtained when the E_c series was shunted with one ohm. This gave a deflection of ten scale divisions, but

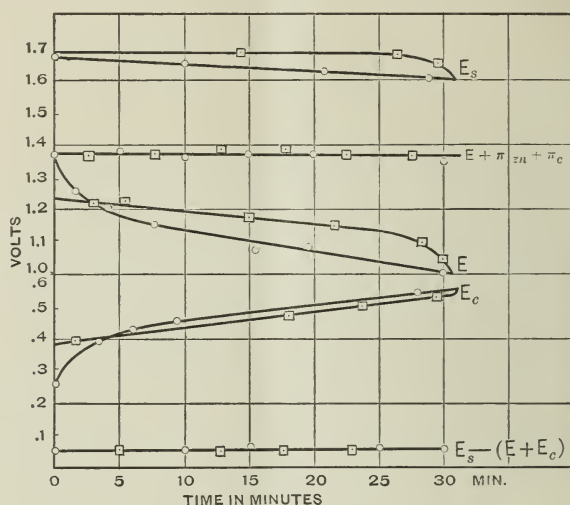


Fig. 2.

it took the series four hours to regain the value first obtained when the battery was upon open circuit, viz., 73 scale divisions. This gives an internal resistance of 6.3 ohms, — a ratio of 1 to 5.5. The current is now, however, three times that in the main circuit with 100 ohms. This difference must be an electrode or contact of electrode and solution phenomena, as the two circuits giving E and E_c are in every respect symmetrical. Streintz¹ has succeeded in measuring the resistance of a cell by means of an alternating current, and finds that the cathode resistance alone shows a dependence upon the current strength, while the anode resistance scarcely varies with the same. As the special carbon is twice cathode in this experiment, the cathode resistance does not help us out. When the main

¹ Wied. Annal., Vol. 57, p. 711, 1896.

carbons are kathode, the internal resistance is smallest, and one would scarcely think that on becoming anode the resistance would be so large. We cannot attribute the difference to polarization, as the difference is marked at the outset when no polarization has occurred.

The chief merit of this method is the means it gives us of determining single potential changes. The curves for E , E_s , and E_c (see Fig. 2) show very decidedly what is taking place. The observations for the polarization are given in the curves by small circles, and the observations for recovery are shown by small squares. It is apparent that the rapid fall of electromotive force at the commencement of a run is to be attributed to polarization at the carbon electrode. Furthermore, the polarization at the zinc electrode cannot be left out of account. The curve shows that the zinc polarization increases uniformly. When the cell is thrown upon open circuit the phenomena are almost exactly reversed. In the first minute of recovery, 18 per cent of the entire loss in electromotive force is regained, and 85 per cent of this gain occurs at the zinc electrode. In five minutes recovery the polarization at the zinc electrode had vanished. The recovery of total electromotive force for the rest of the thirty minutes is due to recovery from polarization at the main carbon electrode. The recovery at the carbon electrode is nearly uniform for thirty minutes. However, the observations are not so decisive as the observations upon the increase of polarization at the zinc electrode. The sum of the observed electromotive force and of the polarization at the two electrodes should be constant and equal to the original electromotive force. We have designated the polarization at the zinc and carbon electrodes by π_{zn} and π_c , respectively, and have drawn a curve showing $E + \pi_{zn} + \pi_c$. This curve is as near a straight line as could be expected. As is apparent, E_s should equal E plus E_c . The curve designated $E_s - (E + E_c)$ shows, however, a constant value equal to 0.054 volts.

Upon the theory of Nernst, we can understand the phenomena here noted. The electromotive force at the zinc electrode is expressed by $\frac{RT}{2c} \log_e \frac{P}{p}$, where R , T , c , P , and p represent the gas constant, absolute temperature, current required to give the one gram-equivalent of the metals, solution pressure, and osmotic pressure of the zinc ions, respectively. Before a current is generated the quantity p is very small. During the action of the cell, the pressure p of the zinc ions would increase at the zinc electrode, and therefore the electromotive force would fall. The ions would of course be more concentrated in the strata nearest to the zinc electrode. The ion first passing into solution would, in a period of thirty minutes, be less than 2 mm. from the electrode. When the cell is thrown upon open circuit, diffusion of the zinc ions occurs. From the



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formula it is apparent that the recovery curve at the zinc electrode should be exponential in character. The observations show that this is probably the case, but the readings of the galvanometer are neither large enough nor frequent enough to demonstrate this character beyond a doubt. At the carbon electrode the gases liberated form a gas battery in opposition to the main circuit. The back electromotive force would increase rather rapidly at first, and later more uniformly. Upon open circuit gas absorption would still continue, and the solution pressure of the gas slowly decrease. It has been shown that the solution pressure of a gas can be expressed by the Nernst formula, and it would scarcely be expected to be as uniform as here noted. However, after standing one hour upon open circuit, the polarization at the main carbon electrode is still apparent, and its magnitude shows that the recovery curve cannot be considered a straight line.

Conclusions.

1. Variation in kathode resistance with current strength does not account for the differences in internal resistance noted in this experiment.
2. Polarization occurs at both electrodes, but is more marked at the carbon electrode.
3. On closing the circuit the rapid fall of electromotive force is due principally to polarization at the carbon electrode.
4. The rapid rise in electromotive force, when a cell is first thrown upon open circuit, is largely due to recovery from polarization at the zinc electrode.

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